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Published in:
Surface and Coatings Technology

Publication date:
2005

Document Version
Early version, also known as pre-print

[Link to publication](#)

Citation for pulished version (HARVARD):
Sadiki, H, Pierson, J, Rousselot, C, Martin, N & Terwagne, G 2005, 'Properties and electrochromic performances of reactively sputtered tungsten oxide films with water as reactive gas', *Surface and Coatings Technology*, vol. 200, no. 1-4, pp. 232-235.

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Properties and electrochromic performances of reactively sputtered tungsten oxide films with water as reactive gas

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Available online 27 April 2005

Abstract

A change of water vapour partial pressure from 0 to 4 Pa was carried out in order to prepare sputtered tungsten oxide compounds with various oxygen and hydrogen concentrations. Oxygen, tungsten and hydrogen concentrations were determined by Rutherford Backscattering Spectroscopy (RBS) and by Elastic Recoil Detection (ERD) analysis. Structure of tungsten oxide films was analyzed by X-ray diffraction. At low water vapour partial pressure, the films are crystallized and WO₂ and W₃O phases were observed. The electrochromic performances of such film/SnO₂/glass substrate system were measured and discussed taking into account the influence of the water vapour partial pressure injected into the deposition process on the structure, chemical composition and optical properties of the films.

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PACS: 68.55.Nq; 78.20-ci; 81.15-cd

Keywords: Reactive sputtering; Tungsten oxide; Electrochromic

1. Introduction

Transition metal oxides have been studied with respect to their electrochromic properties for applications as smart windows, antidazzling mirrors and display devices [1,2]. Since the discovery of the electrochromism phenomenon [3,4], electrochromic layers based on WO₃ have been the most widely investigated oxide in the past.

WO₃ is a cathodic electrochromic material in which the coloration mechanism (from transparent to blue) is generated by the electrochemical reduction. This mechanism is promoted by cathodic polarization, which caused ion insertion and electron injection. The injected electrons are trapped by some W^{VI} sites forming W^V sites, and ions remain ionized in the interstitial sites of the expanded WO₃ lattice. This double injection into the film of WO₃ induces the formation of the tungsten bronze (H_xWO₃) having electronic structure, electrical and optical properties changed in comparison with

single tungsten oxide. Thin films of WO₃ can be prepared by different techniques. Sputtering is one of the most widely used techniques because high-quality films are obtained with higher composition reproducibility. To the best of our knowledge, no study has been devoted to the synthesis of WO₃ films by sputtering methods using water as reactive gas. The introduction of hydrogen-bearing species in the growth process provides the possibility to modify the W valence and to change the transport and electrochromic properties of sputtered-deposited WO₃ films.

In this paper, we report on the use of water vapour as reactive gas to deposit tungsten oxide films. A survey on the effect of water vapour partial pressure on some process parameters is studied first. Structural and chemical composition changes in relation to the optical and electrochromic properties are finally discussed.

2. Experimental

A tungsten target (purity: 99.95%, 50 mm diameter) was DC sputtered with a constant current density $J_W=20 \text{ A m}^{-2}$.

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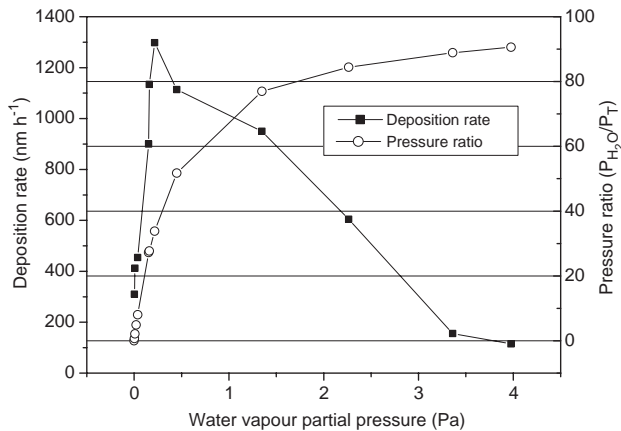


Fig. 1. Deposition rate of tungsten oxide films and pressure ratio vs. water vapour partial pressure at 293 K.

Argon was introduced first up to a pressure $P_{Ar}=0.4$ Pa (constant pumping speed $S=10$ L s⁻¹). Afterwards, the water vapour partial pressure (P_{H_2O}) was changed from 0 to 4 Pa using a leak valve connected to a de-ionised water flask. The pressure ratio (R_{H_2O}) is defined by $R_{H_2O}=P_{H_2O}/P_T$.

The crystallographic structure was investigated by X-ray diffraction using Cu K α radiation ($\lambda=1.5406$ nm) at a grazing angle incidence $\theta=1^\circ$. Optical properties were analysed from optical transmittance spectra of the film/glass substrate system.

Nuclear elemental analyses were performed with ALTAIS, the 2 MV Tandem accelerator installed at LARN. Typical nuclear reactions induced by α -particles were used to measure elemental composition. The experimental details for nuclear analysis have been presented in previous papers [5,6].

The electrochemical measurements were performed using a Tacussel model PGP201 potentiostat and voltamaster 1 pilot software with a three electrodes configuration in a 1.0 M H₂SO₄ solution. The working electrode was glass/SnO₂:F (25 Ω/\square)/WO_xH_y film. A platinum disk and a SCE (Standard Calomel Electrode) were used as auxiliary and reference electrodes, respectively. Cyclic voltammetry was carried out at a rate of 500 mV min⁻¹ and potentiostatic intermittent experiments at voltages between -1.0 to 2.5 V/SCE. The optical density change is defined as $\Delta OD=\log(T_b/T_c)$, where T_b =transmission at 632 nm for the bleached state and T_c =transmission at 632 nm for the coloured state. The coloration efficiency (CE) was calculated from the charge density Q_c (C m⁻²) inserted during the step coloration and calculated according to the following equation $CE=\Delta OD/Q_c$.

3. Results and discussion

3.1. Process

Deposition rate exhibits a maximum (1300 nm h⁻¹) for R_{H_2O} close to 35% (Fig. 1), which corresponds to $P_{H_2O}=0.3$

Pa. Similar results have been obtained by Kaneko et al. [7] and Yamamoto et al. [8] for the deposition of tungsten oxide using O₂ as reactive gas. The evolution of the target potential as function of P_{H_2O} can be explained by the change of sputtering mode. Oxidation rate at the target predominates on the sputtering rate. The difference of molar volumes of components deposited on the substrate can explain the rise of deposition rate if the number of W atoms impinging on the surface is the same. For further increase of P_{H_2O} , the target potential exhibits a drop and reaches a minimum value close to $U_w=390$ V. It probably correlates with an oxidised state of the target. Then, the W-Ar-H₂O process trapped in the oxidised sputtering mode (sputtering yield of tungsten oxide lower than that of metallic tungsten) and the deposition rate decreases from 1300 to 1100 nm h⁻¹. Such a decrease may indicate that the target poisoning starts at low R_{H_2O} and spreads out above 75%. However for ratio higher than 90%, the deposition rate is almost constant, which probably corresponds to a fully oxidised state of the surface of the target. These results reveal that the amount of water vapour required to change the process to oxidised sputtering mode is high because transition is close to $P_{H_2O}=1.5$ Pa ($R_{H_2O}=80\%$). Also, the target potential can be used as a key parameter to

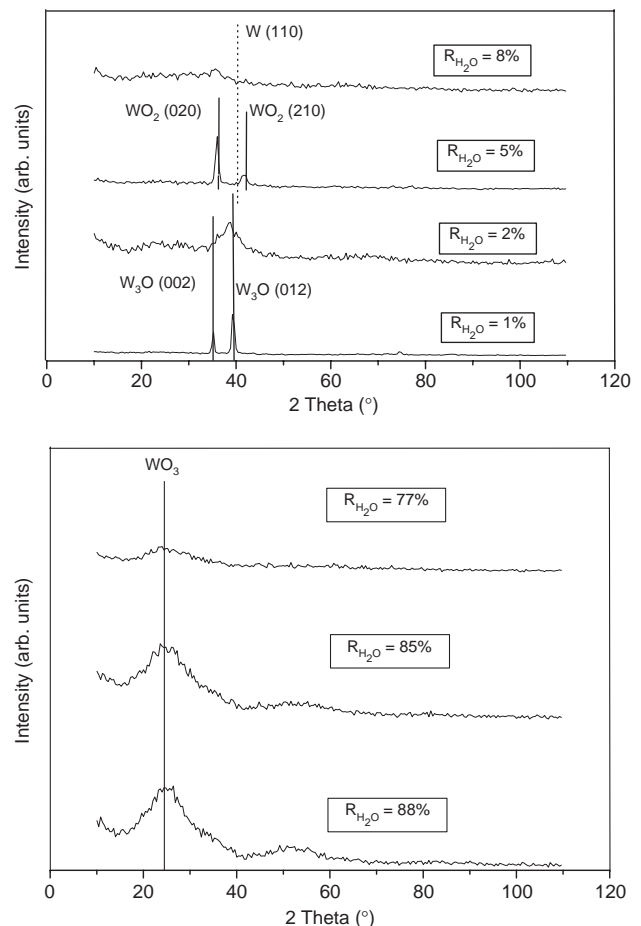


Fig. 2. X-ray diffraction patterns of tungsten oxide films deposited on glass substrate at 293 K for different water vapour pressure ratios.

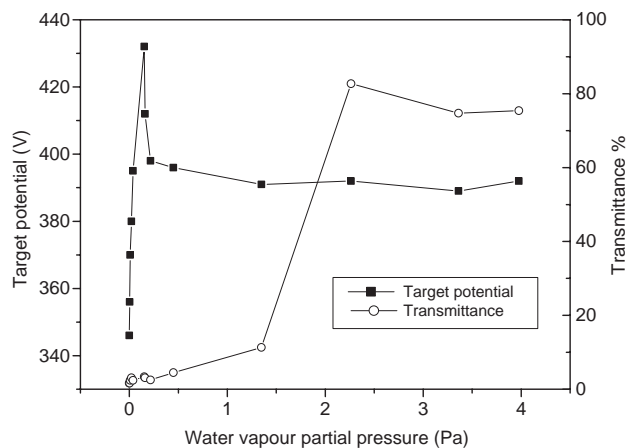


Fig. 3. Tungsten target potential and transmittance at 632 nm of tungsten oxide films vs. water vapour partial pressure.

assess the change of sputtering mode. Transmittance of the films at a wavelength of 632 nm is plotted as a function of $R_{\text{H}_2\text{O}}$ (Fig. 1). It is worth of noting that an increase of the transmittance from 10 to 80% occurs when $P_{\text{H}_2\text{O}}$ changes from 1.3 to 2.2 Pa. Below $P_{\text{H}_2\text{O}}=1.5$ Pa, the films are not transparent and exhibit a typical metallic aspect. Beyond this $P_{\text{H}_2\text{O}}$, which correlates to the transition from metallic sputtering mode to the oxidised one, the films are transparent. This figure proves that the transition of sputtering mode is correlated to the gradual transition of the optical behaviours from metallic tungsten to WO_xH_y compounds.

3.2. Structure and chemical composition

X-ray diffraction patterns of the films show that the crystallographic structure is largely influenced by $R_{\text{H}_2\text{O}}$ in the range of 0–88% (Fig. 2). When $R_{\text{H}_2\text{O}}=1\%$, diffraction peaks corresponding to the W_3O phase (JCPDS no. 41-1230) are clearly observed (Fig. 2a). The W_3O phase is also detected when $R_{\text{H}_2\text{O}}=2\%$. However this $R_{\text{H}_2\text{O}}$ induces a strong refinement of the W_3O grains. This W_3O phase with low oxygen content vanishes when $R_{\text{H}_2\text{O}}$ increases ($R_{\text{H}_2\text{O}}>2\%$). The nature of this oxide phase has been described by several authors [8–10]. Recently, Maillé et al. [10] suggested that the W_3O phase is related to the tungsten target pollution between two sputtering runs when the target is not well cleaned.

At $R_{\text{H}_2\text{O}}$ ranged between 2% and 8%, two diffraction peaks can be assigned to WO_2 phase (JCPDS no. 32-1393). On the other hand, films prepared with $R_{\text{H}_2\text{O}}$ in the 8–77% range exhibits an amorphous structure (Fig. 2b). However, for $R_{\text{H}_2\text{O}}$ higher than 80% (Fig. 3b), we can observe large diffraction peaks, which can be assigned to one of the WO_3 phases with a poor-crystallised structure. This loss of a long range order when $R_{\text{H}_2\text{O}}$ increases can be explained by the lack of energy of particles impinging on the surface of the substrate and their low surface diffusion due to the deposition carried out at room temperature and at high total pressure. These results are consistent with those found by Yamamoto et al. [8] concerning tungsten oxide films deposited by RF sputtering in $\text{Ar}+\text{O}_2$ gas mixture.

The tungsten concentration decreases from 75% to 23%, when $P_{\text{H}_2\text{O}}$ increases from 0.009 to 2.86 Pa. It is in agreement with previous X-ray diffraction results, which indicate the progressive change of the crystallographic structure from W_3O to WO_3 as $R_{\text{H}_2\text{O}}$ increases up to 88%. In addition, a significant amount of nitrogen (higher than 10 at.%) is observed for the lower total pressures (Table 1) which correspond to the experimental conditions to synthesis tungsten oxynitride films. It should be noted that the amount of hydrogen in the films increases with $P_{\text{H}_2\text{O}}$ but it is strongly reduced when the total pressure is high (i.e. $P_{\text{tot}}=3.25$ Pa). At this pressure, the tungsten-based films trap less hydrogen atoms and O/W ratio does not exceed 2.43 (Table 1). On the other hand, for lower total pressure (i.e. from 1 to 1.5 Pa) and with different $R_{\text{H}_2\text{O}}$ included between 80% and 95%, hydrogen concentration reaches 20–25%, O/W ratio tends to 3 and thin films behave as tungsten trioxide compounds with hydrogen as dopant. However, one can notice that the films prepared at a total pressure of 1.5 Pa and with the highest $R_{\text{H}_2\text{O}}$ show the lowest hydrogen content (18 at.%) and O/W ratio (2.33). As a result, the elemental analysis shows that the water vapour can be used as reactive gas to vary the oxygen and hydrogen contents in the films. According to these results, it can be suggested that the high hydrogen contents in the films and the low surface diffusion of the particles without additional heating of the substrate do not favour a well-crystallised WO_3 phase. The hydrogen introduced in the films during the sputtering process prevents the crystal growth of WO_3 phase.

Table 1

Influence of the water vapour pressure on the chemical composition of the tungsten oxide films deposited at 293 K by DC reactive sputtering

P_{T} (Pa)	$P_{\text{H}_2\text{O}}$ (Pa)	$R_{\text{H}_2\text{O}}$ (%)	Thickness (nm)	W (at.%)	N (at.%)	O (at.%)	C (at.%)	H (at.%)	O/W ratio
0.43	0.009	2	210	75	11	2	8	4	0.02
0.56	0.153	27	350	30	12	44	4	10	1.46
0.87	0.45	52	450	25	2	36	2	35	1.44
3.25	2.86	88	650	23	0.1	56	3	18	2.43
1.5	1.20	80	480	18.5	0.1	55	2	25	2.97
1.5	1.27	85	520	18.5	0.1	55	2	25	2.95
1.5	1.42	95	300	24	—	56	2	18	2.33
1.0	0.95	95	400	20	0.1	56	2	22	2.80

Table 2
Influence of the water vapour ratio on the electrochromic characteristics of tungsten oxide films deposited at 293 K by DC reactive sputtering

P_T (Pa)	R_{H_2O} (%)	ΔOD_c	ΔOD_b	OR (%)	Q_c (mC cm ⁻²)	CE (cm ² C ⁻¹)
1.2	85	0.33	0.30	0.92	–	–
1.2	90	0.34	0.14	0.40	11.0	30.9
1.2	95	0.43	0.32	0.76	14.1	30.5
1.5	80	0.74	0.57	0.77	13.8	53.6
1.5	85	0.59	0.39	0.67	13.7	43.1
1.5	90	0.42	0.24	0.58	11.5	36.5

3.3. Electrochromic behaviour

Typical cyclic voltammograms were recorded to measure the coloured state during the cathodic scan (up to -1 V/SCE) and the bleached state during the anodic scan (up to 2.5 V/SCE). The current density and the transmittance at 632 nm measured as well as during the H^+ injected/extracted are used to calculate optical density change of colored state (ΔOD_c) or bleached state (ΔOD_b) as well as charge density (Q_c). The ratio $\Delta OD_b/\Delta OD_c$ is calculated to estimate the optical reversibility (OR) of the film as well as the colouration efficiency (CE). As seen in Table 2, it is found that the electrochromic characteristics of tungsten oxide films are slightly dependent on P_{H_2O} . All tungsten oxide films prepared with high total pressure ($P_T=1.2$ – 1.5 Pa) are hardly electrochemically coloured in blue and exhibit a non optical reversibility. Taking into account the chemical composition of these films (Table 1), we can suggest that high hydrogen content (18–25%) prevents not only the electrochemical colouration but especially the electrochemical bleaching because they remain in the partly coloured state. Since hydrogen atoms in the films take up the interstitial sites, there are not enough available sites to receive H^+ ions injected during the electrochemical colouration.

As a result, tungsten oxide films obtained with $P_T=1.2$ Pa exhibit poor electrochromic properties with CE about 30 cm² C⁻¹ whatever the pressure ratio. On the other hand, for total sputtering pressure higher than 1.5 Pa, the colouration

efficiency tends to the classical value of 60 cm² C⁻¹. However, this colouration efficiency decreases up to 36 cm² C⁻¹ when P_{H_2O} reaches 90%. The electrochromic performances are reduced when water vapour pressure ratio is high.

4. Conclusion

Water vapour was successfully used as reactive gas to deposit electrochromic tungsten oxide thin films by DC reactive sputtering. The target potential can be used to assess the change of sputtering mode when a systematic change of P_{H_2O} occurs during the sputtering process. The tungsten oxide films formed at room temperature with high R_{H_2O} are sub-stoichiometric with O/W ratio lower than 3. They exhibit an amorphous structure with high hydrogen content. At low P_{H_2O} , the films adopt the WO_2 and W_3O structures. Finally, electrochromic measurements demonstrated that it is possible to synthesise electrochromic WO_xH_y films by sputtering with water vapour as reactive gas. However, high hydrogen content in the films favours the non optical reversibility and the fall of the electrochromic performance.

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